

Application of pulsed UV-irradiation and pre-coagulation to control ultrafiltration membrane fouling in the treatment of micro-polluted surface water



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ABSTRACT

A major cause of ultrafiltration (UF) membrane fouling is the accumulation of microorganisms and their associated soluble products. To mitigate fouling the application of pulsed short-wavelength ultraviolet (UVC) light (around 254 nm) within the membrane tank together with pre-coagulation was investigated. In mini-pilot-scale tests carried out in parallel with conventional pre-treatment (CUF), the impact of pulsed UV (CUF-UV) at different UV irradiances and fluxes on the increase of trans-membrane pressure (TMP) was evaluated and explained in terms of the quantity and nature of membrane deposits in the membrane cake layer and pores.

The results indicated that at a flux of $20 \text{ L m}^{-2} \text{ h}^{-1}$, the pulsed UV (1 min within 31 min cycle) at $3.17 \times 10^{-2} \text{ W/cm}^2$ prevented any measureable increase in TMP over a period of 32 days, while there was a fourfold increase in TMP for the conventional pre-treatment. For the CUF-UV system the concentration of bacteria and soluble microbial products was much less than the conventional CUF system, and the cake layer was thinner and contained less biopolymers (proteins and polysaccharides). In addition, the pores of the CUF-UV membrane appeared to have less organic deposits, and particularly fractions with a high molecular weight ($>10 \text{ kDa}$).

At a lower UV irradiance ($1.08 \times 10^{-2} \text{ W/cm}^2$), or higher flux ($40 \text{ L m}^{-2} \text{ h}^{-1}$) with the same UV irradiance, there was a measurable increase in TMP, indicating some fouling of the CUF-UV membrane, but the rate of TMP development was significantly lower ($\sim 50\%$) than the conventional CUF membrane system. Overall, the results show the potential advantages of applying intermittent (pulsed) UVC irradiation with coagulation to control UF membrane fouling.

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1. Introduction

Membrane separation is a rapidly developing treatment technology for the supply of drinking water, but the blockage/reduction of membrane pores, ‘fouling’, caused by particles, organic matter and microorganisms, remains a limitation to its wider application (Lin et al., 2000; Her et al., 2003; Laabs et al., 2006; Huang et al., 2007). Large molecular weight (MW) organic matter such as proteins and polysaccharides can induce significant membrane fouling (Herzberg et al., 2009; Chen et al., 2014). Such hydrophilic

biopolymers are found typically in surface waters used for drinking water supply, and a clear correlation between the concentrations of biopolymers and membrane fouling was observed for surface waters in Japan (Kimura et al., 2015).

Some pre-treatment methods, such as chemical coagulation before membrane filtration, are effective and relatively low cost approaches for improving general water quality and controlling membrane fouling (Peiris et al., 2013; Kimura et al., 2014; Wray et al., 2014). This is partly because coagulation substantially reduces the compressibility of the cake/gel layer (Tabatabai et al., 2014).

As the coagulation process can only remove a proportion of the biopolymers present in raw waters, the remainder can accumulate on the membrane together with those produced by microorganisms in the cake layer. Therefore, an additional treatment method

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before membrane separation is required to more effectively control the membrane fouling. Previously, coagulation and magnetic ion exchange (MIEX) can eliminate the high molecular weight (MW) organic compounds (MW > 20 kDa) attributed to biopolymers (proteins and polysaccharides) that cannot be removed using anion exchange resins alone (Humbert et al., 2007). The use of the MIEX process prior to ultrafiltration, was found to increase the permeate quality, especially for high molecular weight cut-off (MWCO) membranes (Kabsch-Korbutowicz et al., 2008). The combination of coagulation and oxidation as pre-treatment has been widely studied. Recently, various authors showed the potential benefits of applying ozone immediately prior to ultrafiltration (Schlichter et al., 2004; Zhang et al., 2013; Yu et al., 2016). However, the presence of ozone in the membrane tank may gradually cause deterioration of the UF membrane, even resilient PVDF membrane and low ozone doses.

The application of UV irradiation as a pre-treatment for membrane separation is advantageous in view of its well-established capability to mitigate micro-biological activity, and thereby reduce bio-fouling. UV-C (200–280 nm) is effective for bacteria and protozoa spore inactivation and the inactivation may not be affected significantly by the presence of particulates (Li et al., 2009). Recent studies have shown that UV disinfection is effective for inactivating not only total heterotrophic bacteria, but all antibiotic resistant bacteria (Guo et al., 2013), and the inactivation of microorganisms can be described by first-order kinetics using fluence-inactivation data from laboratory studies in collimated beam tests (Hijnen et al., 2006). In a study of membrane bioreactor (MBR) technology, UV disinfection after MBR treatment provided little additional log removal of any organism except for somatic coliphage, whereas UV or chlorine disinfection after conventional secondary treatment provided significant log removal of all bacterial indicators and somatic and F-specific coliphage (Francy et al., 2012). As a membrane pre-treatment, UV irradiation was found to prevent membrane fouling by controlling the microorganism concentration in the feed, and the resulting, continuous running time of the micro-filter membrane was 6 times longer than without UV irradiation (Otaki et al., 1998). Similarly, UV irradiation was reported to be an efficient pre-treatment to reduce nano-filter membrane biofouling (Marconnet et al., 2011).

Pulsed-UV technology has been proposed recently as a rapid, effective method for the disinfection of water and wastewater (Garvey et al., 2014), with a low energy requirement. Initial results from this study indicated that the presence of 10 ppm organic matter did not affect the pulsed-UV inactivation of *Bacillus* endospores at doses exceeding 4.32 $\mu\text{J}/\text{cm}^2$, whereas the presence of organic matter had a significant adverse effect on the inactivation of vegetative cells using standard low-pressure UV at doses >30 mJ/cm^2 (Garvey et al., 2014). In view of the potential advantages of this novel form of UV technology (viz. effective microbial inactivation and low energy), we have evaluated the use of pulsed-UVC light, applied within an ultrafiltration membrane module, together with coagulation, as a method to control membrane fouling. In this

paper we summarize the results of extended-period mini-pilot-scale tests, undertaken under different conditions of UV irradiance and membrane flux, which show a major improvement in membrane performance. The underlying reasons/mechanisms for the improved performance are discussed in detail.

2. Materials and methods

2.1. Model raw water and coagulant

A model water was employed in the tests in order to simulate a micro-polluted surface water and to provide sample consistency and reproducibility throughout the period of membrane operation (~60 days). This was prepared by adding a small quantity of domestic sewage effluent to the local (London, United Kingdom) tap water in a volumetric ratio of 1:50, and 5 mg/L Suwannee River Humic Acid (2S101H, International Humic Acid Substance Society, USA). The addition of domestic sewage effluent and humic acid provided organic matter and microorganisms which are expected to be representative of those found in surface waters. Prior to mixing with domestic sewage effluent and humic acid solution, the tap water was left over night to ensure the complete decay of residual chlorine. The characteristics of the model raw water are presented in Table 1. The temperature of the water was maintained constant at 20 ± 2 °C during the experimental period.

2.2. The treatment processes of ultrafiltration systems

A schematic of the experimental set-up involving the coagulation-UF processes without, and with, the addition of a submersible UVC lamp in the membrane tank (CUF, CUF-UV, respectively), operated in parallel, is shown in Fig. S1. Model raw water was fed into a constant-level tank to maintain the water head for the membrane tanks. An optimal coagulant dose of 0.15 mM $\text{Al}_2(\text{SO}_4)_3$ (calculated as Al), corresponding to a near zero zeta potential of the resulting flocs, was continuously added into the rapid mixing units for each stream. The rapid mix speed was 200 rpm (184 s^{-1}) in the mixing units with a hydraulic retention time (HRT) of 1 min, after which the mixing speed was reduced to 100 rpm (65 s^{-1}), 80 rpm (46.5 s^{-1}) and 50 rpm (23 s^{-1}), respectively, in the three flocculation tanks in series, each having a HRT of 5 min (total flocculation time of 15 min). The flow then passed directly into the membrane tanks, and each tank contained a submerged polyvinylidene fluoride (PVDF) hollow-fiber UF membrane module (Tianjin Motimo Membrane Technology Co., Ltd, China) with a nominal membrane pore size of 0.03 μm and a surface area of 0.025 m^2 . UF permeate was continuously collected by a suction pump at a constant flux during each phase, operated in a cycle of 30 min filtration and 1 min backwash ($40 \text{ L m}^{-2} \text{ h}^{-1}$). For each backwashing, air was supplied at 100 L/h (air: water = 200:1) to each tank in a position underneath the membrane units (Fig. S1), while making sure that the sludge at the bottom of the tanks was retained and not disturbed. The HRT of the membrane tanks was

Table 1
Water quality of raw water and UF systems.^a

Parameter	Raw water	CUF tank	CUF-UV tank	CUF filtrate	CUF-UV filtrate
UV ₂₅₄ (cm^{-1})	0.103 \pm 0.015	0.037 \pm 0.003	0.036 \pm 0.003	0.035 \pm 0.002	0.033 \pm 0.002
DOC(mg/L)	3.52 \pm 0.28	2.73 \pm 0.11	2.55 \pm 0.14	2.40 \pm 0.12	2.32 \pm 0.11
Turbidity(NTU)	3.13 \pm 0.56	4.07 \pm 0.75	5.23 \pm 1.13	0.05 \pm 0.02	0.07 \pm 0.02
NH ₄ ⁺ -N (mg/L)	0.42 \pm 0.09	0.12 \pm 0.03	0.12 \pm 0.03	0.10 \pm 0.02	0.11 \pm 0.02
NO ₃ ⁻ -N (mg/L)	5.67 \pm 0.49	6.07 \pm 0.38	6.04 \pm 0.26	6.08 \pm 0.23	6.05 \pm 0.18
pH	7.97 \pm 0.08	7.67 \pm 0.05	7.53 \pm 0.05	7.67 \pm 0.03	7.51 \pm 0.04

^a The values are averages for all the measurements carried out every 7 days in the first phase.

maintained at 0.5 h and accumulated sludge was released every 2 days. The trans-membrane pressure (TMP) was continuously monitored by pressure gauges. Each membrane unit was taken out from the membrane tank and washed by sponge at day 33 and 46.

For the CUF-UV tank, the UVC lamp with a quartz sleeve was suspended at the bottom of the membrane module. Two lamps were used at different times in the experiments (details below), with a nominal power rating of 10 W and 5 W (Jeneca, China), and their respective energy intensities (irradiance) were determined by radiometry as $3.17 \times 10^{-2} \text{ W/cm}^2$ and $1.08 \times 10^{-2} \text{ W/cm}^2$ at 5 mm distance from the light source. During the period of experimentation each lamp was operated on a cycle of 1 min on and 30 min off, corresponding to the lamp being on during the membrane backwashing; this ensured that the water in the membrane tank was actively mixed while being irradiated by UVC light during the backwash process.

The experiments were carried out in 3 phases in which the flux and UV irradiance were varied, as follows: phase 1 (day 1–32), 10 W lamp and flux = $20 \text{ L/(m}^2 \text{ h)}$; phase 2 (day 32–46), 10 W lamp and flux = $40 \text{ L/(m}^2 \text{ h)}$; phase 3 (day 46–62), 5 W lamp and flux = $20 \text{ L/(m}^2 \text{ h)}$.

2.3. Extraction and measurements of EPS from cake layer and sludge

After each phase of the membrane filtration experiments was finished, the fouled membrane modules were taken out from the membrane tanks. The foulant materials on the membrane surface (cake layer) were carefully scraped off with a plastic sheet, and analyzed by the following methods to characterize their composition; the extraction of internal fouling material is described later.

A heating and extraction method was used to extract the extracellular polymeric substances (EPS; biopolymers) from the settled sludge and cake layers (Morgan et al., 1990; Yu et al., 2015), and to make sure that the EPS was not released from bacterial cells. The method is described briefly as follows. The sludge suspension and cake layers were first dewatered by centrifugation (Model 5417C, Eppendorf, Germany) in a 50-mL tube at 3000 g for 5 min. The sludge pellet in the tube was re-suspended in 20 mL phosphate buffer saline (PBS) solution, sheared by a vortex mixer (Vortex-Genie® 2, Mo Bio laboratories, Inc., USA) for 15 min, ultrasonically treated (Nusonics, USA) for 3 min, and heated to 80°C in a water bath for 30 min. The mixture was centrifuged at 10,000 g for 15 min. The supernatant solution was collected for EPS analysis.

After the membrane surface was wiped with high pressure tap water and a sponge, 0.01 mol/L NaOH was used for the extraction of internal foulants and the fibers were soaked for 24 h at 20°C in the NaOH solution according to the method used and described by many researchers (Kimura et al., 2009; Liu et al., 2011). The extracted organic matter was then subjected to the following chemical analyses. The absolute polysaccharide content in the bound EPS was measured by the phenol–sulfuric acid method with glucose as the standard (Dubois et al., 1956). A modification of the Bradford method (Peterson, 1977) known as the Coomassie procedure (Pierce Chemical) was used to quantify the absolute concentration of proteins, with bovine serum albumin (Sigma) as the standard.

2.4. Characteristics of organic matter

EPS extracted from the cake layers and sludges, and organic matter in the waters from the two membrane systems, were analyzed by SEC based on a unit mass of material after drying, using UV_{254} absorbance (Myat et al., 2014) to determine their apparent molecular weight (MW) distribution of UV-active substances. The

method is described in our previous paper (Yu et al., 2016) and employed a HPLC system (Perkin Elmer, USA), with a Series 200 pump, a BIOSEP-SEC-S3000 column (Phenomenex, UK) ($7.8 \text{ mm} \times 300 \text{ mm}$), and a Security Guard column fixed with a GFC-3000 disc 4 mm (ID).

Resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany) were used to analyze the hydrophilic and hydrophobic organic components by fractionating NOM into three groups: strongly hydrophobic organic matter (adsorbed by DAX-8), weakly hydrophobic (or transphilic) organic matter (adsorbed by XAD-4) and hydrophilic organic matter (passing through both resins) (Aiken et al., 1992; Yu et al., 2016).

2.5. Other analytical methods

Fouled membrane fibers were cut from the two membrane modules, and care was taken to retain the foulant layer attached on the membrane surface. The fouled membrane samples were then platinum-coated by a sputter and observed under high resolution field emission gun scanning electron microscope (FEGSEM, LEO Gemini 1525, Germany). Also, the new and fouled membrane samples were analyzed by Fourier Transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA) with Quest ATR Accessory (SPECAC Ltd, UK).

The UV absorbance at 254 nm, UV_{254} , of $0.45 \mu\text{m}$ filtered solutions was determined by an ultraviolet/visible spectrophotometer (U-3010, Hitachi High Technologies Co., Japan). Dissolved organic carbon (DOC) was determined using a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu, Japan). Turbidity measurements were made using a commercial turbidimeter (Hach 2100, USA), and the concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were determined by the colorimetric method using a spectrometer (APHA, 2005); suspended solids (SS) concentrations were also quantified by APHA (2005). The concentration of bacteria was determined as the Heterotrophic Plate Count (HPC) by the yeast extract agar method (ISO6222, 1999).

The DNA in the cake layer and sludge were extracted following the procedures given by the extraction kit employed in this work (Fast DNA® Spin kit for soil, Lot, 19,744, MP, USA), and which is described elsewhere (Zhang and Fang, 2000). The DNA contents were measured by UV absorption at 260 nm (NanoDrop 2000 spectrophotometer, Thermo Scientific, USA). The method used for soluble microbial products (SMP) can be found in the review by previous researchers (Kunacheva and Stuckey, 2014).

3. Results and discussion

3.1. Variation of TMP

The coagulation-UF processes without, and with, the addition of UVC light in the membrane tank (CUF and CUF-UV) were operated over 60 days in three phases. The development of membrane fouling, as indicated by changes in the TMP, for the different systems is shown in Fig. 1. For the first phase of operation (up to 31 days), the TMP of the CUF membrane unit gradually increased to 8.3 kPa, while the CUF-UV system displayed no significant TMP increase. The results indicated that under these conditions UV irradiation prevented the development of membrane fouling that was observed with coagulation pre-treatment alone (CUF), as a consequence of reduced bacterial presence and breakage of residual large MW organic matter. After physical cleaning of the membranes (by high pressure tap water and sponge wash) at day 32, the TMP of the cleaned CUF membrane was much greater ($\sim 4.2 \text{ kPa}$) than that of the new membrane ($\sim 2 \text{ kPa}$). The lack of any detectable increase of TMP for the CUF-UV membrane showed the absence of

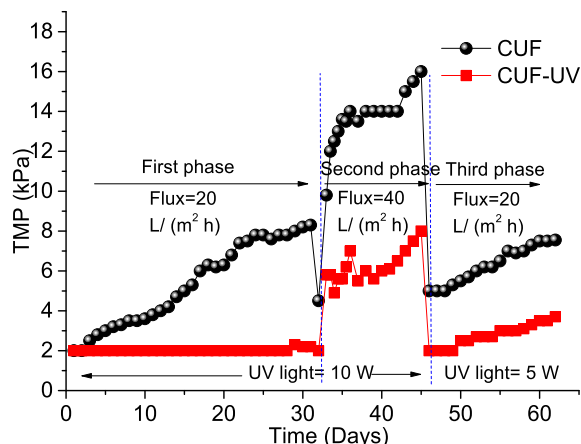


Fig. 1. Influence of UVC irradiance and membrane flux on the variation of TMP in the two membrane systems during the three phases of operation (experimental conditions for each phase shown in the figure).

any internal and external membrane fouling for the CUF-UV membrane during the first stage of operation and the effectiveness of the combined coagulation-UV pre-treatment.

During the second phase of testing, the membrane flux was increased to 40 L/(m² h), but with the same UVC irradiance. The TMP increased quickly in both systems as a consequence of doubling of the flux. The increase rate of TMP in the CUF system (~0.48 kPa/day) was much greater than for the first phase (~0.19 kPa/day), confirming the general observation that higher membrane flux increases membrane fouling (Bacchin et al., 2006). For the CUF-UV system the greater membrane flux led to a significant increase in the temporal TMP development (~0.23 kPa/day) in marked contrast to the lack of any measurable increase during the first phase (~0 kPa/day). After the initial, proportional rise in TMP owing to the change in flux through the clean membrane (~4.5 kPa), the subsequent increase in TMP was more gradual, but less than the rise for the CUF membrane; for the period between days 34 and 45 the rise in TMP was approximately 3 kPa for the CUF-UV and 6 kPa for the CUF membranes. After physical cleaning of the membranes at day 46, the TMP of the cleaned CUF membrane was slightly higher (~4.9 kPa) than that after the first wash (~4.2 kPa), suggesting some increase in deposits within the membrane pores. In contrast, the initial TMP for the CUF-UV membrane at the beginning of phase 3 was not measurably different to that at the beginning of phase 1 for the new membrane (2 kPa).

For the third phase (days 46–63), the membrane flux was decreased back to 20 L/(m² h), but the UV irradiance was reduced by replacing the 10 W lamp with the 5 W lamp. For the CUF membrane the rate of change of TMP was the same as in phase 1, as expected, while the TMP in the CUF-UV system was observed to steadily increase, unlike in phase 1 at the higher irradiation level, although at a rate approximately half that of the CUF membrane. The results of the three phases clearly demonstrate the importance of the UV irradiance and flux on the development of membrane fouling. In the following sections, the influence of the UV irradiation on particle variation and microbial activity, and thus the external and internal membrane fouling, was further investigated.

3.2. SS, bacteria and SMP concentration in the membrane tanks

The formation process of cake layers on the surface of the membrane requires particles and their adhesive (like bricks and cement for a house), and here these can be represented by suspended solids (SS) and soluble microbial products (SMP)

concentrations, respectively. The cake layer on the membrane surface is gradually formed by the accumulation of suspensions/particles (SS) present in the influent flow (i.e. flocculated water) of the membrane tanks.

As shown in Fig. 2a, the SS concentrations were significantly greater within the two membrane tanks than the raw water. These were assumed to accumulate during the flow residence time in the membrane tanks and from the membrane backwashing. However, the SS concentration in the CUF-UV tank was greater than that in the CUF tank, particularly in phase 1, even though the bacteria concentrations were lower (Fig. 2b). The SS values represent the combination of poorly settling coagulant flocs and micro-organisms (mainly bacteria), and membrane cake material released during backwashing. The biopolymers released by the bacteria, represented by the EPS/SMP concentration, may be beneficial in the formation of settleable coagulant flocs and in the adhesive strength of the cake layer. Therefore, during phase 1 when the bacteria concentration in the CUF-UV tank was suppressed by the UV irradiation, it is speculated that the absence of sufficient biopolymers (Fig. 3b) to enhance settleable floc formation and cake adhesion, led to the greater SS concentration observed compared to the CUF tank. A similar behavior was evident in phases 2 and 3 where lower bacterial levels resulting from the UV irradiation in the CUF-UV system corresponded to higher SS concentrations (cf. CUF). The greater SS concentration for both membrane systems in phase 2 can be explained by the reduced flow residence time arising from the greater flux, hence less opportunity for floc sedimentation, and greater cake layer solids released from

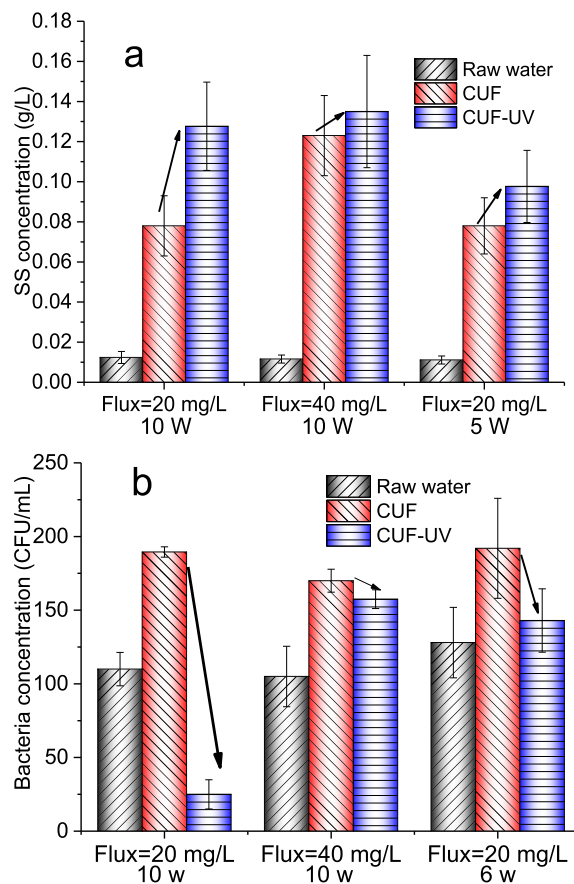


Fig. 2. Average concentrations (sampled at the middle of cycle) of suspended solids (a) and bacteria (b) in the membrane tanks, with and without UVC irradiation for the three different phases.

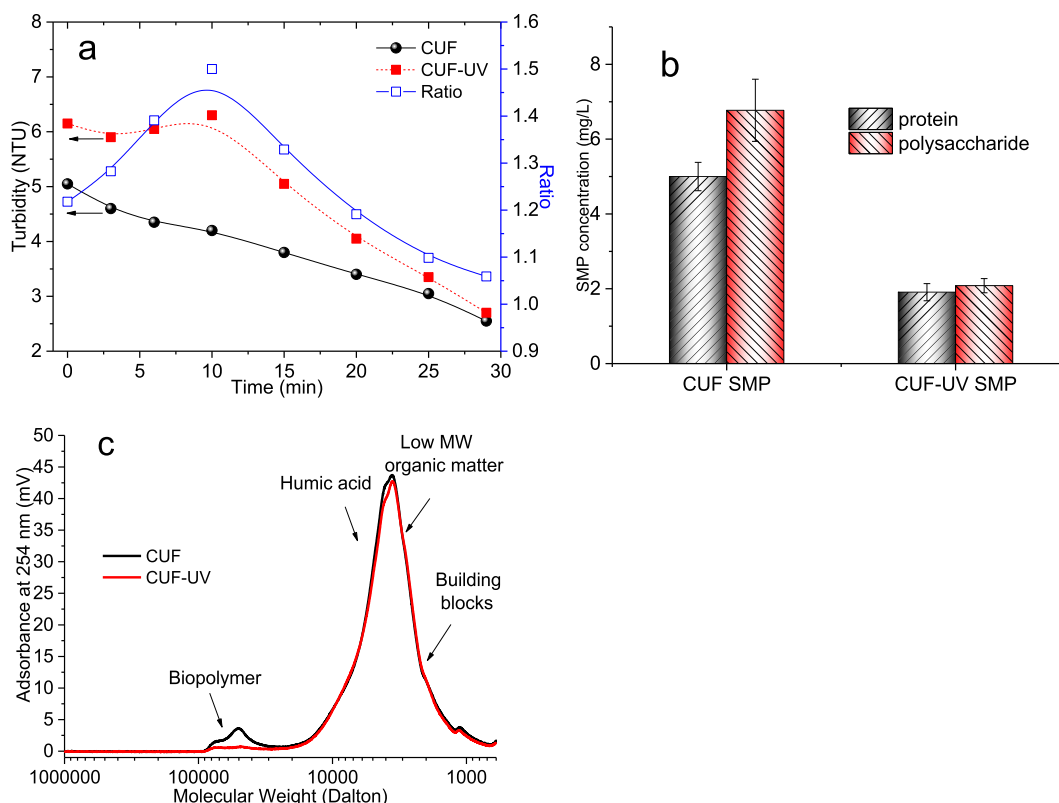


Fig. 3. Turbidity variation (a) during one membrane filtration cycle (30 min), SMP concentration (b) and molecular weight of organic matter (c) extracted from the particles in the membrane tanks at day 20 (first phase).

backwashing. In phases 2 and 3, the bacteria concentrations were lower for the CUF-UV system than the CUF, indicating the effect of UVC light, particularly in phase 3; the greater bacteria numbers in phase 3 compared to phase 1 for the CUF-UV membrane is consistent with the reduced UV irradiation in the former, while the greater bacteria numbers in phase 2 may reflect the reduced flow residence time (UV exposure) compared to phase 1. Therefore, it can be seen that the overall presence of bacteria within the CUF-UV membrane system is determined by the combined effects of flow residence time (bacterial growth and separation by settling) and UV inactivation.

The variation of turbidity within the membrane tanks during the operating cycles (i.e. 30 min filtration and 1 min backwash) was explored to understand the behavior of the particles in suspension, comprising those washed away from the cake layer and new/existing particles present within the membrane tank; the results for the first phase are summarized in Fig. 3. It was evident that particles gradually settled after the backwash event and it required 10 min for the particles in the CUF-UV tank to settle from the top of tank to the sample points (Fig. 3a). For the CUF tank, the lower initial turbidity and gradual decrease indicated that the particles were difficult to remove from the cake layer owing, it is suggested, to their greater cohesiveness and adhesion to the membrane surface, partly caused by the existence of EPS/SMP materials. As the turbidity/SS concentration at the end of each operation cycle was the same for the two systems, it is clear that different quantities/numbers of particles were detached from the cake layers of the two membrane systems during backwashing. The fact that the affinity between particles in the cake layer was greater in the CUF system suggests that UV probably reduces the bonding capacity of suspensions (particles) in the membrane tank to the membrane

surface (cake layer and/or membrane fiber) through the EPS produced by the bacteria. Comparing the results of SMP concentrations determined in the membrane tanks, it was found that both protein and polysaccharide concentrations were substantially higher in the CUF tank than the CUF-UV tank (Fig. 3b). The relative presence of biopolymers in general from SEC analysis further confirmed that the application of UVC light led to lower SMP/biopolymer concentrations in the membrane tank (Fig. 3c), thereby resulting in less particles being attached to the membrane surface. This observation that a greater EPS concentration in the CUF tank enhanced the adhesion ability of suspensions onto the membrane surface, has also been observed previously in the context of wastewater treatment (Tsuneda et al., 2003).

3.3. Characterisation of organic matter in the membrane tanks during the first phase

Organic matter within the membrane tank has the capability to accumulate in the UF membrane pores gradually during the operation cycle, inducing internal fouling. Therefore, the characteristics of the organic matter in the membrane tanks were evaluated, such as the degree of hydrophilicity and thermal decomposition profile (TGA method).

The results concerning the hydrophilic properties showed that much of the strongly hydrophobic organic matter was removed by the coagulation process, and little hydrophilic matter was removed (Fig. 4a). More strongly hydrophobic organic matter was removed in the CUF-UV tank, compared to the CUF tank. As hydrophobic organic matter is easier to be adsorbed onto the hydrophobic PVDF membrane pores, UVC irradiation can improve the removal of hydrophobic organic compounds and thereby mitigate inner

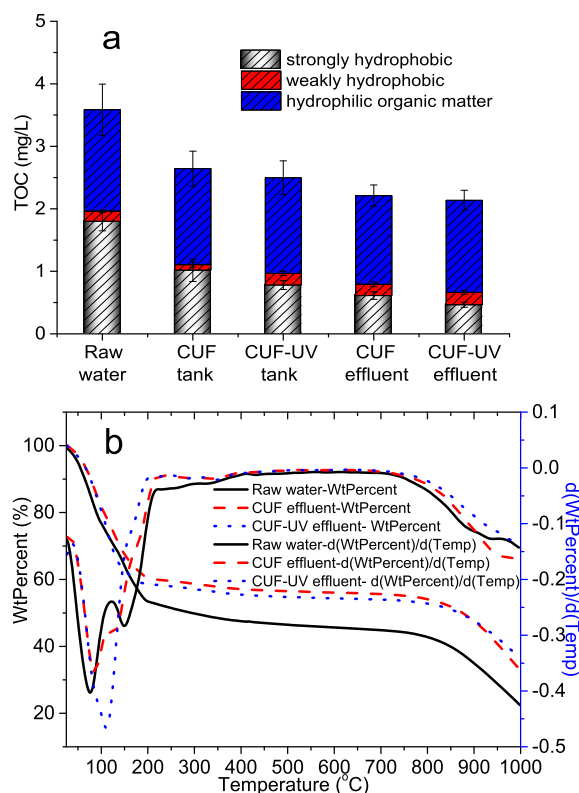


Fig. 4. Proportion of hydrophilic and hydrophobic components (a) and TGA profile (raw water and membrane effluents) (b) of organic matter from water in the membrane systems during the first phase.

membrane fouling.

Also the organic matter (after freeze drying from water) was characterized by thermogravimetric (TG-DTA) analysis (Fig. 4b). The TG-DTA analysis revealed that organic weight loss occurred principally at temperatures in the ranges of 50–250 °C and higher than 700 °C. In general terms there was a greater weight loss for the raw water NOM compared to the membrane effluents, mainly in the temperature range up to 250 °C. In the lower temperature range (50–250 °C), the specific weight loss ($d(Wt\%)/d(Temp)$) of the raw water NOM had two peaks at about 70 °C and 160 °C, while for the CUF effluent the maximum specific weight loss was at a temperature of approximately 70 °C and 130 °C; thus the behavior of the CUF sample was similar to the raw water, but with lower weight loss (as organic matter was removed by the coagulation process). For the CUF-UV effluent, the maximum specific weight loss was near 110 °C, which indicated that less large MW organic matter was produced in the CUF-UV tank. These results further highlighted significant changes in the nature of the organic matter, resulting from lower bacterial inactivation and less EPS, as a result of the application of the pulsed UVC light during the UF pre-treatment stage.

3.4. External fouling

The cake layer that forms on the membrane surfaces comprises flocculated particles that incorporate organic matter, bacteria and EPS, and differences in the nature of the cake layer with, and without, pulsed UV were investigated. Images of the cake layer of fouled UF membranes and their cross-sections, at different phases,

were obtained by SEM (Fig. 5). A thick deposit layer was evident on the surface of the membranes consisting of thousands of deposited colloidal particles, formed from precipitated nanoparticles with adsorbed organic matter on their surfaces. Images of the membranes from the CUF and CUF-UV systems at day 32 (first phase) suggested a greater porosity of the cake layer for the CUF-UV membrane (Fig. 5a and b), possibly because the connection strength between particles in the CUF-UV cake layer was lower than the CUF system because of less EPS concentration (Tsuneda et al., 2003); in contrast, there was little difference in the appearance of the cake layers for the following two phases (data are not shown).

The SEM images also showed that the thickness of the cake layer on the surface of the membranes was different in the two systems for the different phases. In the first phase (day 32), it can be seen clearly that the CUF cake layer was nearly three times thicker than the CUF-UV layer (Fig. 5c and d), while for the second and third phases (e.g. Fig. 5e and f), the thickness of the CUF cake layer was only slightly greater than the CUF-UV layer, indicating that the intensity of the UVC light (phase 3) or the irradiation contact time (phase 2) was insufficient. Thus, in phase 1 it is believed that the reduced level of EPS/biopolymer in the CUF-UV system corresponded to a weaker cake layer that could be more easily removed by backwashing, and a lower attachment efficiency of particles onto the surface of the cake layer or membrane, thereby resulting in a reduced thickness of the cake layer in the CUF-UV system compared to the CUF system. In contrast, for the second and third phases, the reduced contact time or lower UVC intensity, respectively, corresponded to much less inactivation of bacteria, and resulting in a similar extent of cake layer formation to the CUF system. Support for these observations was provided by the results of EPS and DNA concentrations in the cake layer, as follows.

Comparing the EPS content extracted from the cake layers in the two systems for the first phase, the concentrations of protein and polysaccharide in the CUF system were considerably greater than those in the CUF-UV system (Fig. 6a and b). In contrast, for the second phase and third phase, there were minor differences (within experimental variation) in the protein and polysaccharide concentrations between the CUF and CUF-UV tanks. Similarly, the results of the DNA analysis showed that the quantity of DNA in the CUF cake layer was approximately double that in the CUF-UV cake layer during the first phase (Fig. 6c), while for the second and third phases, the differences in DNA between the two systems was much less. Overall, the results for microbial DNA were consistent with the previously discussed results for bacterial numbers (Fig. 2b), SMP (Fig. 3b) and EPS (Fig. 6a/b) in terms of the comparison between the CUF and CUF-UV systems over the three phases.

In addition to the measurements of the EPS and DNA concentrations in the cake layers, the nature of the organic matter in the cake layers was investigated in terms of the MW distribution (as determined by SEC) to further explain the differences in membrane fouling for the three phases (Fig. 7). The results show that the quantity of organic matter in the CUF system was greater than in the CUF-UV system for all three phases. As most of the organic matter had a MW smaller than 20 kDa, and the pore size of the UF membrane was approximately 100 kDa, this fraction of the organic matter would not induce membrane fouling significantly. However, the presence of higher MW fractions corresponding to biopolymers (EPS), between 50 kDa and 100 kDa, was significantly greater in the CUF system than that in the CUF-UV system during the first phase, but not so in the second and third phases. From this it is concluded that the relative absence of biopolymers in the CUF-UV system in phase 1 contributed to the low level of fouling observed, while

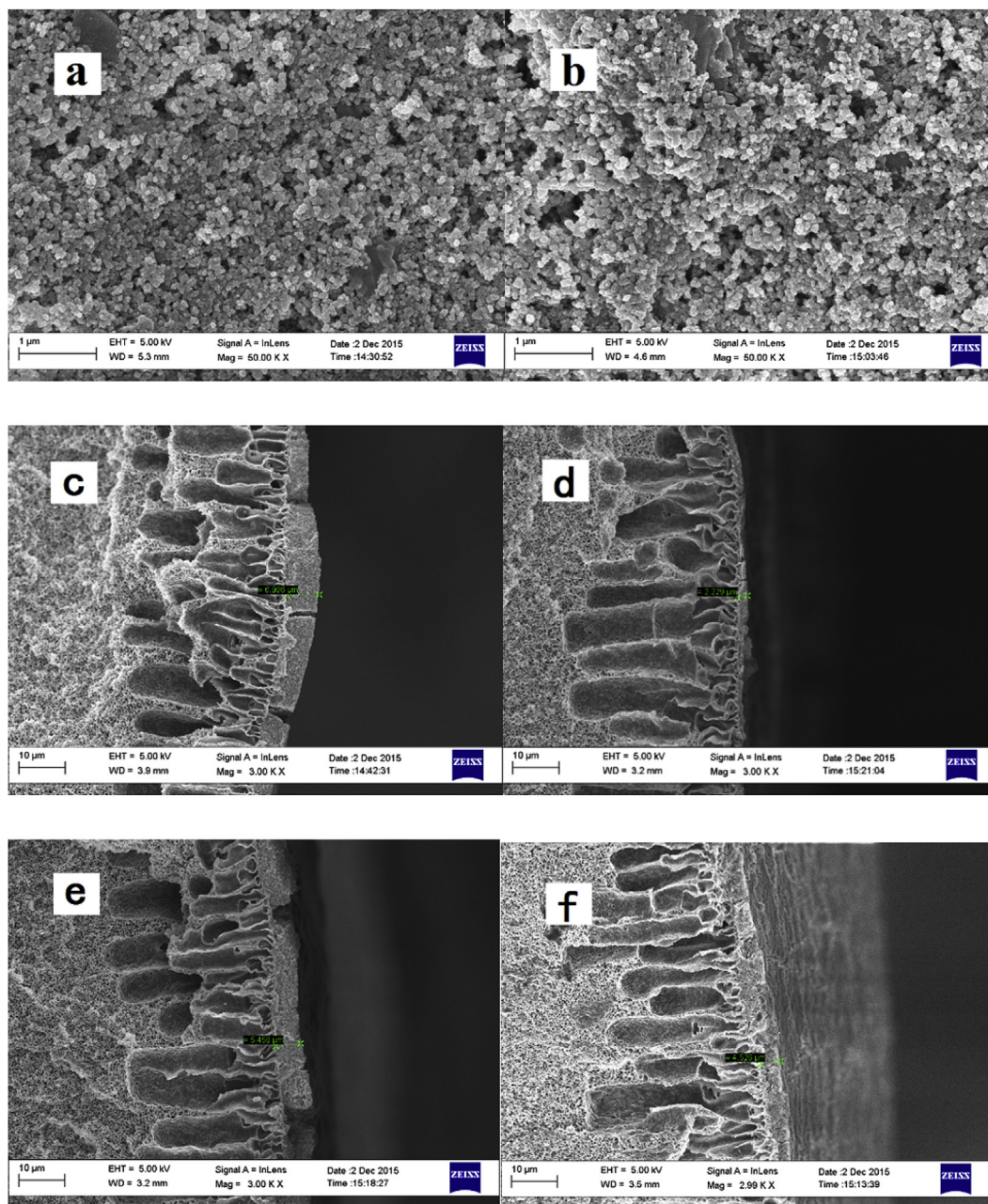


Fig. 5. SEM images of fouled membrane with cake layer (external membrane fouling): (a) CUF membrane and (b) CUF-UV membrane at day 32 (end of first phase); cross-section of CUF membrane (c) and CUF-UV membrane (d) at day 32 (end of first phase); cross-section of CUF membrane (e) and CUF-UV membrane (f) at day 63 (end of third phase).

conversely, the much greater presence of biopolymers in phases 2 and 3 for both the CUF and CUF-UV systems led to substantial external membrane fouling (TMP).

3.5. Internal membrane fouling

Images of the membrane surfaces were taken by SEM after the cake layer was removed from the membrane surface, to investigate the extent of internal membrane fouling (Fig. 8). It can be seen that few large pores were evident on the CUF membrane surface and the statistical number of pores was very small, compared to the CUF-UV membrane surface (Fig. 8b and c), although both membranes were severely blocked. In addition to the blockage of pores, the adsorption of organic matter within the membrane was greater for the

CUF membrane, as indicated by the accumulation of small particles, and the rugged appearance (Fig. 8e and f). These observations are consistent with the increased initial TMP evident for the CUF membrane for phases 2 and 3 (Fig. 1), corresponding to internal, irreversible fouling.

Accumulated material extracted from internal membrane pores was analyzed by SEC (Fig. 9). It can be seen that significantly less organic matter was retained or adsorbed in the CUF-UV membrane pores, compared to the CUF system, especially the higher MW material ($>10^4$ Da), such as biopolymers and humic-like substances. These results complement the visual evidence from the SEM images, described above, which highlight the beneficial impact of the pulsed UVC light pre-treatment on internal membrane fouling.

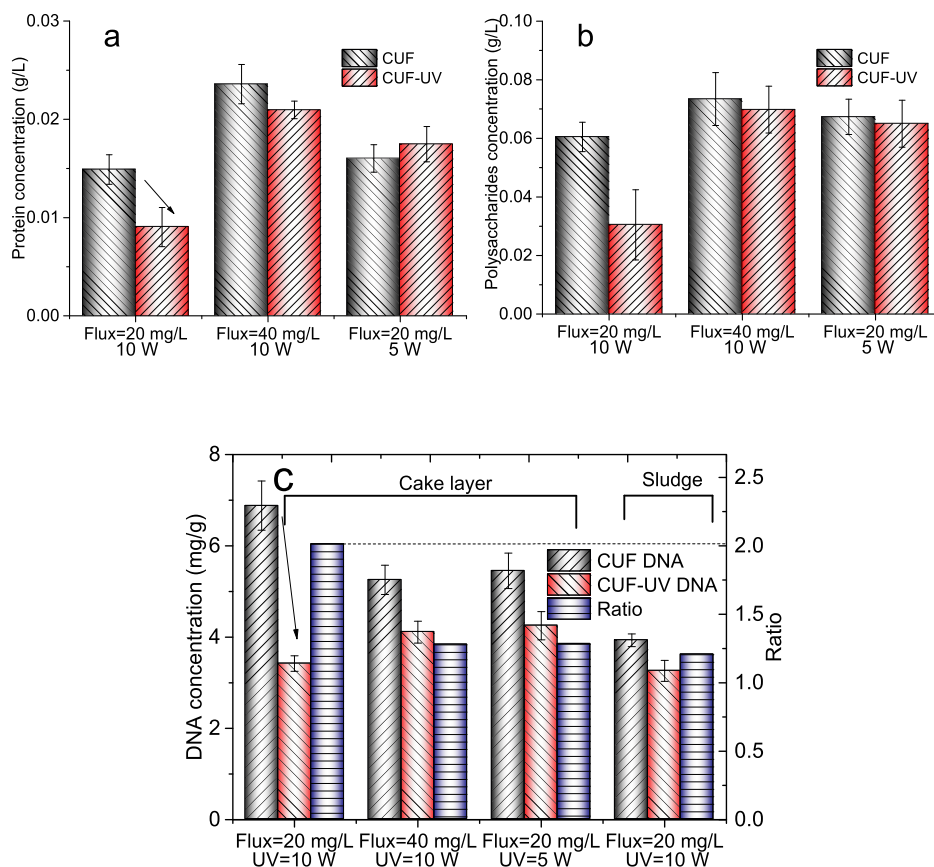


Fig. 6. EPS and DNA concentration in the cake layer or sludge during the three operational phases: a) protein and b) polysaccharide in the cake layer, c) DNA concentration in the cake layer or sludge.

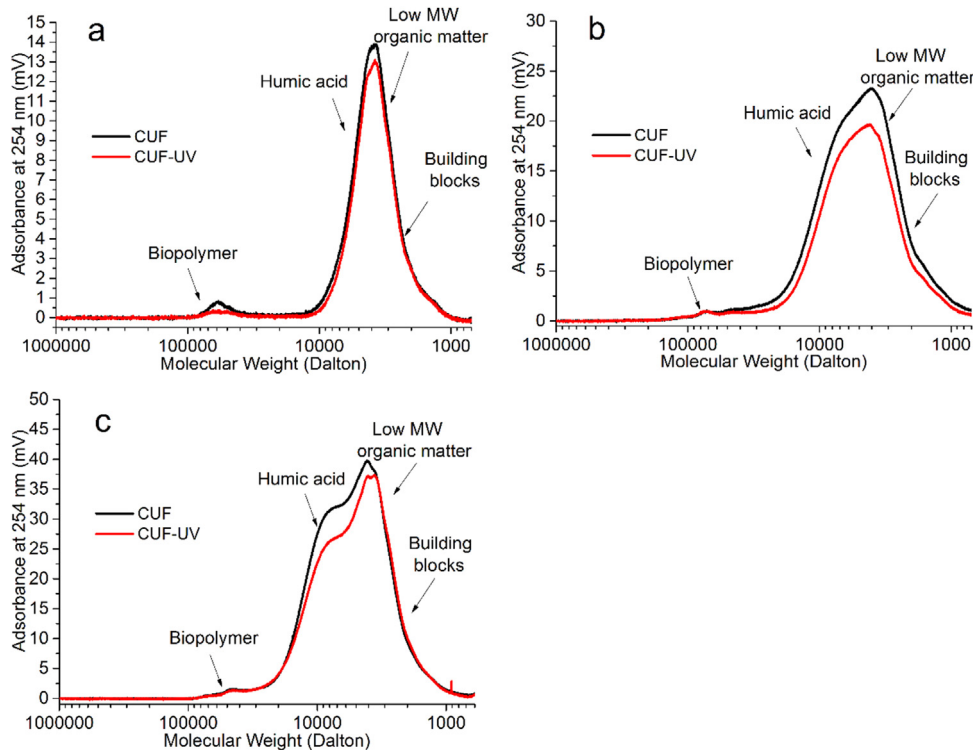


Fig. 7. MW distribution of organic matter extracted from cake layer: (a) first phase (flux 20 L/m² h and 10 W UVC light), (b) second phase (flux 40 L/m² h and 10 W UVC light), and (c) third phase (flux 20 L/m² h and 5 W UVC light).

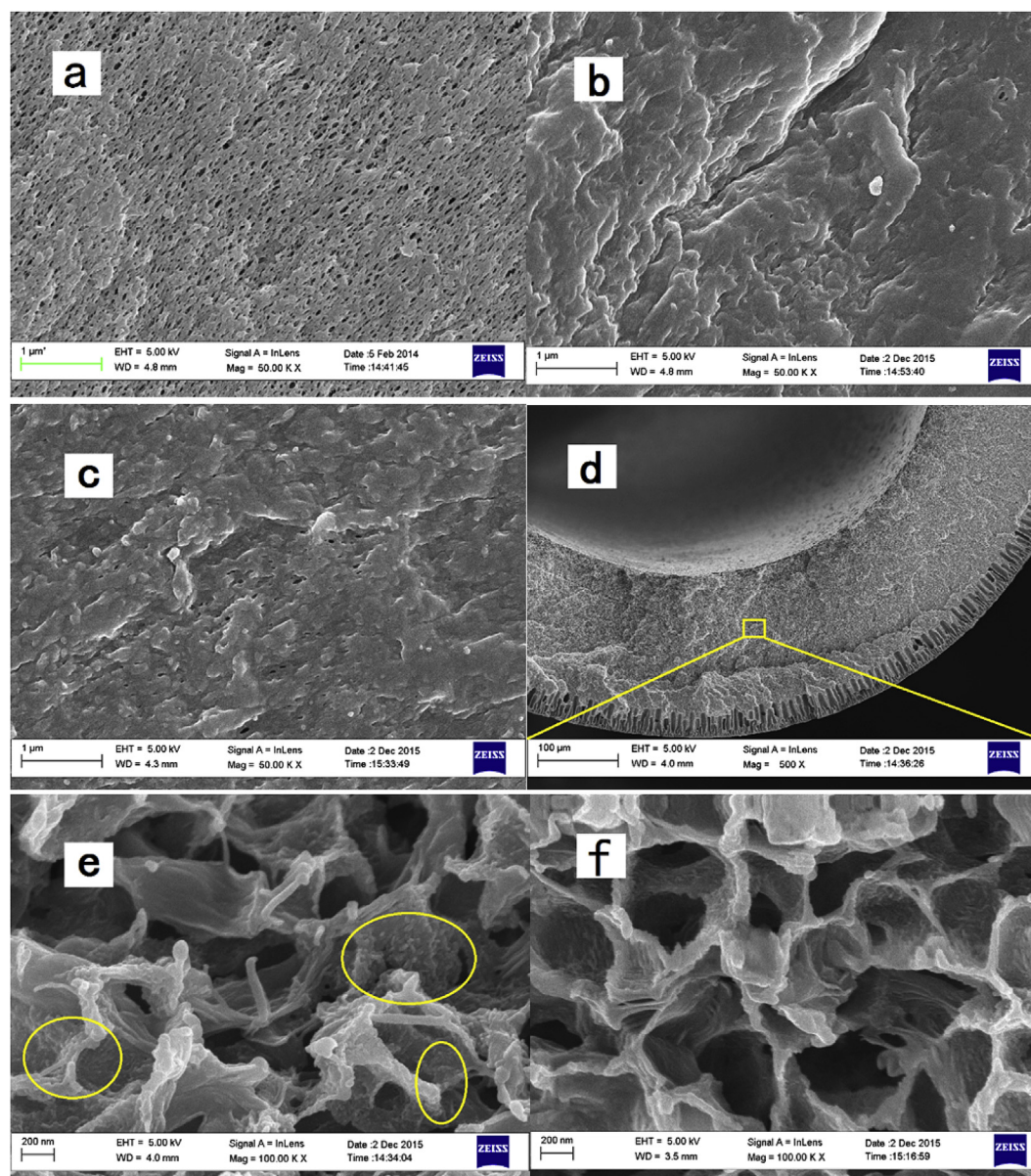


Fig. 8. SEM images of fouled membrane without cake layer (internal membrane fouling) at day 62: (a) new membrane, (b) CUF membrane and (c) CUF-UV membrane; cross-section of membrane (d): CUF membrane (e) and CUF-UV membrane (f) in the inner membrane.

4. Conclusions

This study has evaluated the performance of a novel combination of intermittent (pulsed) UVC irradiation and coagulation as a method of preventing UF membrane fouling. Alternative operating conditions in terms of the applied UV irradiance and membrane flux have been considered, and the results have shown the following:

1 UVC light with enough contact time and intensity in the membrane tank could prevent measurable membrane fouling over an operational period of 32 days. Under less favorable conditions (lower UVC intensity and higher flux), the combination of UV irradiation and coagulation was still able to mitigate membrane fouling compared to the conventional pre-treatment.

2 The application of pulsed UVC substantially reduced the concentration of bacteria and EPS within the membrane tank, and

this corresponded with a thinner, more porous cake layer that contained lower concentrations of bacteria and EPS compared to the membrane with conventional pretreatment. It is speculated that the cake was weaker owing to the absence of binding substances (e.g. EPS) enabling it to be more easily removed during backwashing.

3 Under less favorable conditions (lower UVC intensity and higher flux), the porosity, thickness and biopolymer content of the CUF-UV cake layer became similar to the CUF layer, which was consistent with the moderate extent of fouling observed, although the rate of TMP development was less for the CUF-UV membrane system.

4 Internal (irreversible) fouling induced by the deposition within, or blockage of, membrane pores by organic matter was considerably greater for the CUF membrane; however, the presence of such deposits within the pores of the CUF-UV membrane

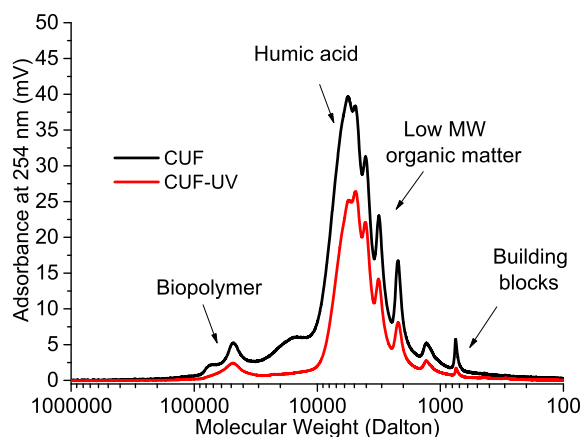


Fig. 9. MW distribution of organic matter extracted from membrane pores of the two membrane systems (day 63).

were sufficiently minor that they had no measurable impact on the initial TMP.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.10.058>.

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